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(21) International Application Number: PCT/IT89/00063 (22) International Filing Date: 19 September 1989 (19.09.89) (30) Priority data: 48406 A/88 30 September 1988 (30.09.88) IT (71) Applicant (for all designated States except US): F.P.S. ITALIANA - FINANCES PRODUCTS SERVICES S.R.L. [IT/IT]; Via Guglielmo Oberdan, 119, I-95100 Catania (IT). (72) Inventor; and (75) Inventor/Applicant (for US only) : ZANUCCOLI, Pietro [IT/IT]; V. Musumeci, 123, I-95128 Catania (IT). (74) Agents: BANCHETTI, Marina et al.; Ing. Barzanò & Zardo Roma S.p.A., Via Piemonte, 26, I-00187 Rome (IT).		(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SULFUR-BASED CHEMICAL SOIL-CORRECTIVE IN THE FORM OF PELLETS FOR AGRICULTURAL USE (57) Abstract A sulfur-based, chemical soil-corrective or conditioner for agricultural use in the form of pellets, said product containing fly sulfur powder, at least 3 % by weight of an inert compound selected from the group consisting of clay, bentonite, kaolin and mixtures thereof, and at least 0.5 % by weight of a wetting agent; said components are mixed with one another, then subjected to wet extrusion and next to drying, so as to obtain mechanically strong pellets which are porous and suitable to be very easily dis-aggregated when they are in contact with soil moisture.		

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SULFUR-BASED CHEMICAL SOIL-CORRECTIVE IN THE FORM OF
PELLETS FOR AGRICULTURAL USE

This invention relates to a sulfur-based chemical soil-corrective for agricultural use, said product being in the form of pellets. More particularly this invention relates to a pellettized sulfur-containing chemical soil-corrective or soil-conditioner (i.e., a fertilizer whose main function is that of correcting the constitutional deficiencies of an agricultural soil), whose pellets, though sufficiently strong to resist mechanical stresses so as to be handled without undergoing crumbling, are rapidly dissolved when in contact with soil moisture so that powder sulfur becomes available in a short time.

As is well known, sulfur is supplied to soil with the main object of correcting alkalinity of the same and of intervening in the sodium-calcium ionic exchange. In agricultural soils, elements like nitrogen, phosphorus or potassium are to be supplied to soil in amounts of the order of tons or of quintals per hectare (macroelements) according to the kind of cultivation, while other elements like copper, zinc, manganese, iron etc. (microelements) are required in amounts just of the order of grammes or kg per hectare; as a fertilizer, sulfur is considered to be a mesoelement, which is to be supplied in some hundred kg per hectare according to the kind of cultivation; on the contrary, as a corrective-acidifying agent, sulfur is a macroelement, to be administered in amounts of tons per hectare according to the alkalinity of the soil or to the presence of sodium.

Once sulfur is present in soil in finely divided form, it is converted into sulfate ions by sulfoxidizing microorganisms, like the

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bacteria of the kind Thiobacillus.

Not much care has been taken in general up to the present time of introducing sulfur directly into the soil, as the sulfur requirement was already satisfied by sulfate-containing fertilizers, as well
5 as by acids rains and by the employment of natural organic manures with high contents of such element.

With the decrease in the employment of such manures and the lowering the concentration of sulfuric acid in acid rains, the need for making up for lack of sulfur is increased in the recent times.

10 It is quite evident that the best form for a rapid availability of the sulfur to bacterial attack, owing to its water insolubility, is the powder form; more particularly it has been set forth that the average granulometry should be lower than 80 mesh.

However, powdered sulfur cannot be easily distributed over
15 soils because it gets easily dispersed into the air and it is irritant, so that it gives rise to inconvenience and troubles to workmen, especially as regards the eyes.

In order to obviate such drawbacks, some granular products have been prepared that can be easily distributed both by hand and by
20 means of mechanical devices without dispersions into the air. In such products sulfur is mixed with bentonite clay by means of a hot process; the clay should make the granule disgregation easier when it is in contact with water, because it swells when exposed to moisture. Actually, such granules disgregate to a small extent essentially
25 because of the fact that sulfur, which is insoluble and compact within the granule, "protects" the clay, so that the latter can contact water only after part of the sulfur has been removed from the granule due to the direct bacterial attack. It is evident that a compact pellet of some millimetres in diameter exposes a very limited surface to
30 bacterial attack if compared to the same amount of sulfur powder or

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even sulfur in the form of a porous granule.

The drawback mentioned above stems mainly from the fact that the disclosed granular products are obtained through hot processes, starting from molten sulfur. The granule so obtained, even though it contains up to 10% of swelling clay, is hard and compact, and solidified sulfur prevents the same from being water-degraded. Accordingly, the products in question require long times for being assimilated by the soil.

Therefore, the object of the present invention is to provide a sulfur-based soil-corrective which is easy to handle just like the granular products already known, but which at the same time can also rapidly disgregate in soil water, so that the sulfur can expose a much larger surface to the aggressive attack of soil microorganisms.

To that aim, the invention provides a new kind of pellets based on fly sulfur powder containing also clay and a wetting/dispersing agent, the powders of the three components being mixed with one another, then made into a paste with water, and the resulting mix being subjected to extrusion and to a final drying. The resulting pellets are mechanically strong and not easily subject to crumbling when dry, and once put in contact with water they are quickly degraded, thus liberating in a short time sulfur in the form of a powder.

The advantageous performance of the product according to the present invention is due both to the presence of additional ingredients in said mix and to the particular wet-process employed for preparing such product starting from sulfur powder, which process does not involve the melting and the subsequent solidification of the sulfur particles.

The clay, which can be partially or totally substituted with bentonite and/or kaolin, performs the function of a binding agent in

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the mix and, in the finished product, it performs the well known function of swelling once it is in contact with water, so as to be of aid in causing the pellet to be disgregated. In the mix together with sulfur, the wetting agent and water, clay also performs the functions of a lubricating agent for extrusion, as it makes the mix much more easy to process.

Moreover, when the pellets so obtained are dried, the mixture as a whole does not shrink, but clay, by liberating water, contributes to the creation of a network of pores throughout the granule, said pores making the penetration of water and the consequent disgregation of the granule remarkably easier.

The wetting/dispersing agent clearly performs the function of allowing the water-repellent sulfur powder to be wetted and, additionally, it acts as an adhesive in the mix once the same has been dried, so preventing it from flaking off.

Accordingly, the present invention specifically provides a sulfur-based soil-corrective for agricultural use in the form of pellets, which product contains fly sulfur powder, at least 3% by weight of an inert product selected from the group consisting of clay, bentonite, kaolin and mixtures thereof, and at least 0.5% by weight of a wetting agent, the components being mixed with each other and being subjected to wet extrusion and subsequent drying to obtain said pellets.

The wetting agent is preferably selected from among lignin sulfonates or residual sugar products like distillation residues or slops; otherwise such agent can be any suitable solid or liquid surface active agent, or a mixture of two or more of the agents mentioned above.

A preferred embodiment of the product according to the present invention is that containing about 93% by weight of fly sulfur

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powder, 5% by weight of clay and 2% by weight of lignin sulfonate.

Moreover, other inorganic compounds can also be added to the mixture, such as for instance gypsum, magnesium sulfate or potassium sulfate. In that case, as a portion of sulfur is already present in the form of the sulfate ion, it is possible to lower the contents of elemental sulfur. Moreover, gypsum has the further advantage of containing the calcium ion for the Ca-Na ionic exchange in soil.

Other fertilizers in the form of powders can also be added to the mixture of the present invention, so as to complete the composition of the same. More particularly, compounds containing macro- and/or meso- and/or microelements can be added, or other organic manures or amending products and/or wastes from agricultural-food industries can be added, such as exhausted husks, exhausted grapes skins, citrus fruit peels, tomato skins, by-products of the distillation industries, and so on.

The addition of microelements like copper, zinc, manganese, magnesium, iron, boron, molybdenum etc. to the product of the present invention is also particularly useful, said product acting as a vehicle for such elements, so that their separate distribution in soil in the minimum amounts required is avoided.

The addition of phosphorus-based compounds can also be of particular advantage, as the presence of sulfur favours the dissolution of insoluble phosphorus, so making easier the absorption of such element by the plants.

According to a specific procedure for preparing the corrective product of the present invention, the components in the form of powders are mixed with one another, or better they are crushed and milled together in order to favour the homogenization of the mix. Then water is added in amounts about equal to the weight of clay plus the wetting agent that are being employed, and the mix is fed to a

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die drawplate by means of rollers or by a screw feeder, which also causes further mixing of the paste, thus making the same more homogeneous. After extrusion, the product is passed through an air stream, so that it dries, thus giving the desired pellets.

5 Alternatively, hemihydrate calcium sulfate or anhydrous magnesium sulfate can be employed in the mix mentioned above as drying agents. The first one of said compounds, in addition to act as a fertilizer, also has the property of absorbing one part of water per five parts of the material, while the second one can absorb one
10 part of water per about one part of material.

 As already mentioned above, the pellets are solid and strong, and they do not crumble or become crushed during handling, but their microscopic structure is highly porous, and as soon as they are in contact with the soil moisture they are rapidly disgregated so
15 liberating sulfur powder, so that sulfur becomes quickly available for bacterial attack and for its transformation into the sulfate ion.

 This invention has been disclosed with specific reference to some preferred embodiments thereof, but it is to be understood that modifications and/or changes can be introduced by those who are
20 skilled in the art without departing from its true spirit and scope.

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CLAIMS

1. A sulfur-based chemical soil-corrective in the form of pellets for agricultural use, said product comprising fly sulfur powder, at least 3% by weight of an inert product selected from the group consisting of clay, bentonite, kaolin and mixtures thereof, and
5 at least 0.5% by weight of a wetting agent, said components being mixed with one another and subjected to wet extrusion and subsequent drying to obtain said pellets.

2. A product according to claim 1, wherein said wetting agent
10 is selected from the group consisting of lignin sulfonates, sugar compounds, distillation residues or slops, and surface active agents.

3. A product according to claim 2, wherein said wetting agent is a lignin sulfonate.

4. A product according to anyone of the preceding claims 1-3,
15 said product also containing gypsum and/or potassium sulfate and/or magnesium sulfate.

5. A product according to anyone of the preceding claims 1-4, said product also containing other fertilizing components.

6. A product according to claim 5 wherein said fertilizing
20 components are macro- and/or meso- and/or micro-elements.

7. A product according to claim 5 wherein said fertilizing components are organic fertilizers.

8. A product according to claim 3, containing 93% by weight of fly sulfur powder, 5% by weight of clay and 2% by weight of lignin
25 sulfonate.

9. A product according to anyone of the preceding claims, in the form of pellets of 1-10 mm diameter and 1-10 mm length.

INTERNATIONAL SEARCH REPORT

PCT/IT 89/00063

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.C1. 5 C05D9/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.C1. 5	C05D ; C05G ; C01B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	DE,B,1592609 (DEUTSCHE HYPERPHOSPHAT GMBH) 26 February 1970 see column 3, line 6 - column 4, line 35; claims	1-7, 9
A	---	8
Y	DE,B,1024934 (BADISCHE ANILIN- & SODA-FABRIK AG) 27 February 1958 see column 3, line 5 - column 4, line 21	1-3
Y	US,A,3062637 (J.O. MARPLES ET AL.) 06 November 1962 see column 3, lines 67 - 75 see column 4, lines 14 - 17 see column 4, lines 56 - 69 see column 5, lines 11 - 27 see column 6, lines 59 - 70; claims	1
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<p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
13 DECEMBER 1989	DEC 13 1989	
International Searching Authority	Signature of Authorized Officer	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	GB,A,499807 (E. I. DU PONT DE NEMOURS AND CO.) 27 February 1939 see claims ---	2
Y	DE,A,2601677 (R.L. REPERT) 21 July 1977 see page 3, lines 10 - 16; claims ---	1, 4-7, 9
A	US,A,1795364 (CARLETON ELLIS) 10 March 1931 see claims ---	1
A	US,A,4062694 (E.W. SAWYER, JR) 13 December 1977 see claims ---	1
A	FR,A,1511002 (POTASSE & ENGRAIS CHIMIQUES) 26 January 1968 see claims ---	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

IT 8900063

SA 31423

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-B-1592609	26-02-70	None	
DE-B-1024934		None	
US-A-3062637		None	
GB-A-499807		None	
DE-A-2601677	21-07-77	None	
US-A-1795364		None	
US-A-4062694	13-12-77	None	
FR-A-1511002		None	